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Synthesis and Electrophilic Cyclization Reactions of Diphenyl 3-Methylhexa-1,3,4-trien-3-yl Phosphine Oxide

Ivaylo K. Ivanov and Valerij Ch. Christov

Department of Organic Chemistry & Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, BG-9700 Shumen, Bulgaria

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ABSTRACT: *Diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide can be readily prepared via an atom-economical 2,3-sigmatropic rearrangement of the mediated alkenynyl phosphinite formed in situ by a reaction of 2-methylhex-5-en-3-yn-2-ol with diphenylchlorophosphine. Electrophilic cyclization reactions of prepared 1-vinylallenyl phosphine oxide were investigated as it was established that the reactions proceeded with formation of heterocyclic compounds with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring group participation of the phosphoryl and/or vinylic group.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–7, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21023

INTRODUCTION

The presence of two π electron clouds separated by a single sp-hybridized carbon atom is the identifying structural characteristic of allenes, and it is this unique structural and electronic arrangement that is responsible for the extraordinary reactivity profile displayed by allenic compounds [1]. The synthetic potential of functionalized allenes has been explored extensively in recent years, and this has led to the development of novel methods for the construction of a variety of functionalized heterocyclic and carbocyclic systems [2].

One of the characteristic reactions of the allenes is the electrophilic addition reactions in which the addition products of the reagent to the one and/or other double bond of the allenic system are usually obtained [3]. Functionalized allenes are very interesting substrates as a material of choice to study the electrophilic addition reactions on the carbon–carbon double bonds [4–6]. Unlike the allenic hydrocarbons, the presence of a functional group linked to the allenic system considerably changes the course of the reactions with electrophilic reagents. It has been shown [4–6] that the reactions proceeded with cyclization of the allenic system bearing a functional group give heterocyclic compounds in most cases. It makes the investigations on the functionalized allenes, more specifically in studying their reactions with electrophilic reagents, quite an interesting and topical task.

Recently, we have developed the electrophilic cyclization reactions of 1- and 3-vinylallenyl sulfoxides [7] and sulfones [8]. In all the cases, the electrophilic atom has been introduced to the central carbon atom of the allene moiety and the reactions proceeded with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring group participation of the sulfinyl (sulfonyl) and/or vinylic group [7,8].

The literature data on the electrophilic addition reactions to phosphorylated allenes (phosphonates,

Correspondence to: Valerij Ch. Christov; e-mail: vchristo@shu-bg.net.
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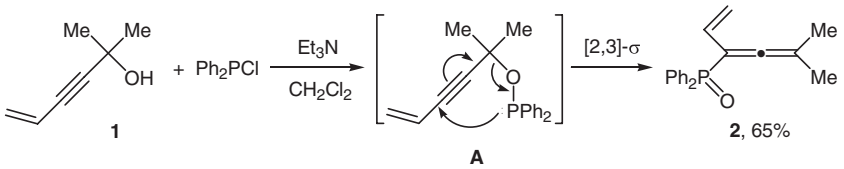


SCHEME 1

phosphinates, and phosphine oxides) show that various five-membered heterocyclizations proceed in most cases [4,6,9–12]. On the other hand, the reactions of 1,2,4- and 1,3,4-alkatrienephosphonates with electrophiles lead to the synthesis of various heterocyclic compounds. For example, the halogenation reactions afford 3- or 5-vinyl-substituted 2,5-dihydro-1,2-oxaphospholes [13,16], whereas the interaction with sulfenyl [14,16] and selenenyl [15,16] chlorides gives thiophene- or selenophene-2- or 3-phosphonates. Reactions of diphenyl 3-methylpent-1,2,4-trienyl phosphine oxide with electrophiles proceeded with formation of various heterocyclic or highly unsaturated compounds [17].

There are methods [18] for the synthesis of phosphorus-containing allenes (phosphonates [19], phosphinates [20], and phosphine oxides [21]), including reactions of α-alkynols with chloride-containing derivatives of phosphorus acids followed by a [2,3]-sigmatropic rearrangement.

As a part of our long-standing program on the synthesis and cyclization reactions of sulfur- and phosphorus-functionalized vinylallenes, we now report the results on the synthesis of diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide and the reactions with some electrophilic reagents for the study of the electrophilic cyclization reactions.

RESULTS AND DISCUSSION

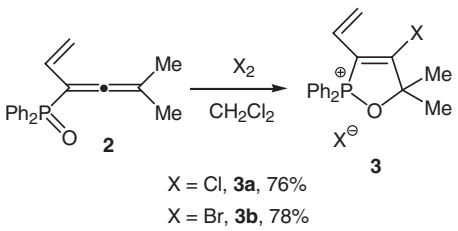
Since its discovery five decades ago [19a,20a,20b], the reversible interconversion of propargylic P(III) esters (phosphites, phosphonites, and phosphinites) to allenyl phosphonates, phosphinates, and phosphine oxides has become one of the most studied and synthetically useful 2,3-sigmatropic rearrangement. Numerous synthetic applications of the rearrangement have been reported, including its use in the synthesis of allenic steroids as substrate-induced inactivation of aromatase [22a], in the efficient synthesis of (2*R*)-2-amino-5-phosphonopentanoic acid as a powerful and selective *N*-methyl-d-aspartate antagonist [22b], in the preparation of the phosphonate analogues of phosphatidyl derivatives [22c,22d], and, in the synthesis of new acyclic analogues of nucleotides containing a purine or pyrimidine moiety and an allenic skeleton [22e,22f].

Our strategy for the synthesis of diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2**, using our experience on the preparation of the vinylallenyl sulfoxides [7] and sulfones [8] relies on the well-precedented 2,3-sigmatropic shift of propargylic phosphinites to allenyl phosphine oxides [21].

Diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2** can be readily prepared via an atom-economical 2,3-sigmatropic rearrangement of the mediated alkenynyl phosphinite **A** formed in situ by a reaction of 2-methylhex-5-en-3-yn-2-ol **1** with diphenylchlorophosphine in the presence of triethylamine according to Scheme 1.

1-Vinylallenyl phosphine oxide **2** isolated in preparative amounts allowed us to study its chemical behavior in the reactions with electrophilic reagents. From general considerations as well as from the literature data on the electrophilic addition reactions [23] to phosphorylated allenes [4], 1,2,4- and 1,3,4-alkatrienephosphonates [13–16], 3-vinylallenyl phosphine oxide [17], vinylallenyl sulfoxides [7], and sulfones [8], the following pathways of the reactions could be assumed:

I. attack of the reagent on the C^4–C^5 double bond with formation of 4,5-adduct;
II. attack of the reagent on the C^3–C^4 double bond with formation of 4,3- and/or 4,1-adduct;
III. attack of the reagent on the C^4–C^5 double bond of the trienic system and following neighboring group participation of the internal nucleophile (phosphoryl group) and ring closure to a five-membered cyclic compound;
IV. attack of the reagent on the C^3–C^4 double bond of the trienic system and following neighboring group participation of the C^1–C^2 double bond and ring closure to the cyclic compound;
V. attack of the reagent on the C^1–C^2 double bond with formation of 1,2- and/or 1,4-adduct; and
VI. elimination reactions after realization of some of the above-mentioned pathways (I–V).



SCHEME 2

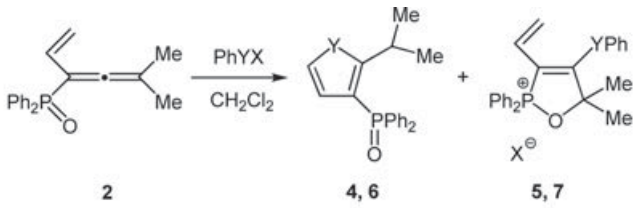
We initially examined the halogenation reaction of diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2**. According to our previous experimental results on the electrophilic cyclization reactions of functionalized vinylallenes [7,8,17], dichloromethane was a good solvent for electrophilic addition reactions to allenes. When CH_2Cl_2 was used as the solvent, diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2** reacted with sulfuryl chloride or bromine at $-20^{\circ}C$ to give 4-halo-2,2-diphenyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium chloride **3a** or bromide **3b** in 76% and 78% yield, according to the reaction sequence outlined in Scheme 2.

Obviously, the electrophilic halocyclization reaction occurs by neighboring group participation of the phosphine oxide group with formation of the five-membered cyclic products **3**.

Surprisingly, the reaction of 1,3,4-trienyl phosphine oxide **2** with benzenesulfanyl chloride or bromide proceeds with two types of electrophilic cyclization by neighboring group participation of both the vinylic double bond and the phosphine oxide group to give mixtures of 3-(diphenylphosphinoyl)-2-isopropyl-thiophene **4** and 2,2-diphenyl-4-phenylsulfanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium chloride **5a** or bromide **5b** in 65% and 69% overall yields according to the sequence outlined in Scheme 3.

In a similar way, ca. 3.8:1 mixture of 3-(diphenylphosphinoyl)-2-isopropyl-selenophene **6** and 2,2-diphenyl-4-phenylselanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium chloride **7a** or bromide **7b** was obtained with 67% and 63% overall yield from the reaction of 1-vinylallenyl phosphine oxide **2** with benzeneselanyl chloride or bromide in dry dichloromethane at $-20^{\circ}C$ as outlined in Scheme 3.

The obtained compounds **6** and **7a, b** contain the isotope ^{77}Se, which is magnetically active and interacts with other nuclei. This interaction becomes evident with the protons and carbons of the neighboring groups, which exhibit symmetric satellite signals of the main signal in the ^{1}H and ^{13}C NMR spectra [24].

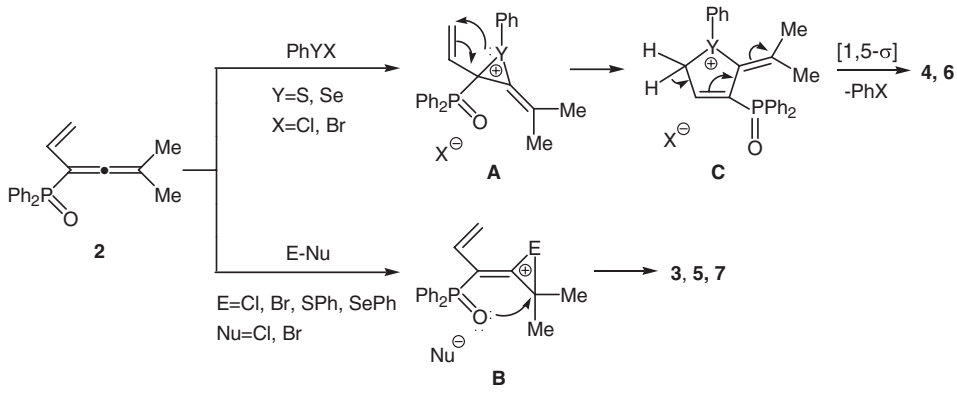


Y	X	Yield (%)				Ratio
		4	5	6	7	
S	Cl	55	**5a**, 14	–	–	3.93 : 1
S	Br	52	**5b**, 13	–	–	4.0 : 1
Se	Cl	–	–	53	**7a**, 14	3.79 : 1
Se	Br	–	–	50	**7b**, 13	3.85 : 1

SCHEME 3

Our results on the electrophilic halo-, sulfano-, and selano-cyclization reactions of 1-vinylallenyl phosphine oxide **2** are in contrast to Ma and coworkers' studies on the electrophilic iodohydroxylation [9], fluorohydroxylation [10], and selenohydroxylation [11] reactions of allenyl phosphine oxides with iodine, Selectfluor, and benzeneselanyl chloride affording 2-iodo(respectively, 2-fluoro, or 2-phenylselanyl)-3-hydroxy-1(*E*)-alkenyl phosphine oxides with high regio- and stereoselectivities, which the authors [9–11] believed to be determined by the neighboring group participation effect of the diphenyl phosphine oxide functionality.

On the basis of previous results [7,8,17], a plausible mechanism is proposed (Scheme 4). The initial act is the attack of the electrophile (X^+, S^+, or Se^+) on the most nucleophilic atom of the trienic system of π-bonds (C^4) with the formation of two cyclic onium (halogenonium, thiiranium, or seleniranium) ions **A** and **B** after attacks on the relatively electron-rich C^4–C^5 (in all cases) and C^3–C^4 (in the case of sulfanyl and selanyl electrophiles only) double bonds, respectively. The ions **A** are in the plane of the π-bond of the vinyl group (*s*-cis conformation), and for this reason **A** are easily transformed into the more stable five-membered cyclic ions **C**. Furthermore, the ions **C** undergo elimination of phenyl halide, 1,5-prototropic shift, and aromatization to give thiophene **4** or selenophene **6**. The five-membered cyclic phosphonium chlorides and bromides **3**, **5**, and **7** are formed via neighboring group participation of the oxygen atom of the diphenyl phosphine oxide functionality in the stage of ion **B** formation.



SCHEME 4

The simultaneous realization of the both heterocyclization processes is connected with introduction of the allenic and 1,3-dienic parts of the trienic system into the reaction course. This fact is obviously due to the ability of the halogens, sulfur, and selenium to form cyclic ions [25], which are further transformed into five-membered heterocyclic compounds.

CONCLUSIONS

We note the following points from this investigation:

1. Diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2** can be readily prepared via an atom-economical 2,3-sigmatropic rearrangement of the mediated alkenynyl phosphinite formed in situ by a reaction of 2-methylhex-5-en-3-yn-2-ol with diphenylchlorophosphine.
2. Electrophilic cyclization reactions of 1-vinylallenyl phosphine oxide **2** were investigated as it was established that the reactions proceeded with formation of various heterocyclic compounds with participation of the allenic and/or 1,3-dienic part of the vinylallenic system with neighboring participation of the phosphoryl and/or vinylic group;
3. Diphenyl 3-methylhexa-1,3,4-trien-3-yl phosphine oxide **2** is a versatile synthone for heterocyclic compounds in organic synthesis. Owing to the importance of phosphine-containing compounds, both as reagents and ligands, as well as due to the presence of carbon–carbon double bonds, carbon–heteroatom (halogen, sulfur, selenium) bond, and five-membered heterocyclic moiety, this reaction shows its potential and will be useful in organic synthesis. Further studies on the score, the synthetic applications of this reaction, and the physiological activity of selected heterocyclic products are now under investigation in our laboratory.

Furthermore, a continuation of these studies toward the synthesis and electrophilic cyclization reactions of other functionalized vinylallenes is currently in progress in our laboratory.

EXPERIMENTAL

General

All new synthesized compounds were purified by column chromatography and characterized on the basis of NMR, IR, and microanalytical data. NMR spectra were recorded on a DRX Bruker Avance-250 (Bruker BioSpin GmbH, Karlsruhe, Germany) (^{1}H at 250.1 MHz, ^{13}C at 62.9 MHz, ^{31}P at 101.2 MHz) and Bruker Avance II+600 (^{1}H at 600.1 MHz, ^{13}C at 150.9 MHz, ^{31}P at 242.9 MHz) spectrometers for solutions in $CDCl_3$. Chemical shifts are in parts per million downfield from internal TMS. *J* values are given in hertz. IR spectra were recorded with an FT-IRAffinity-1 Shimadzu spectrophotometer (Shimadzu Corp., Japan). Elemental analyses were carried out by the Microanalytical Service Laboratory of Faculty of Chemistry, University of Sofia using Vario EL3 CHNS(O) (Elementar Analysensysteme GmbH, Hanau, Germany). Column chromatography was performed on Kieselgel F_{254}60 (70–230 mesh ASTM, 0.063–0.200 nm, Merck). The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. Reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for purity on TLC plates Kieselgel F_{254}60, Merck.

Starting Materials

Benzenesulfanyl chloride was prepared from diphenyl disulfide and sulfuryl chloride in

dichloromethane and distilled in vacuo (bp 80–81°C/20 mmHg) before use [26]. Benzenesulfanyl bromide was freshly prepared from diphenyl disulfide and bromine in dichloromethane and used without purification. Benzeneselanyl bromide was freshly prepared from diphenyl diselenide and bromine in dichloromethane and used without purification. 2-Methylhex-5-en-3-yn-2-ol, benzeneselanyl chloride, diphenyl disulfide, and diphenyl diselenide were commercially available and were purified by usual methods.

*Synthesis of Diphenyl 3-Methylhexa-1,3, 4-trien-3-yl Phosphine Oxide (**2**)*

To a solution of 2-methylhex-5-en-3-yn-2-ol **1** (3.30 g, 30 mmol) and triethylamine (3.34 g, 33 mmol) in dry dichloromethane (50 mL) at −70°C, a solution of freshly diphenylchlorophosphine (6.62 g, 30 mmol) in the same solvent (20 mL) was added dropwise with stirring. The reaction mixture was stirred for 2 h at the same temperature and for 3 h at rt and then washed with water (50 mL), 2 N HCl, extracted with dichloromethane, and the extract was washed with saturated NaCl, and dried over anhydrous sodium sulfate. Evaporation yielded the crude product **2**, which was purified by column chromatography on silica gel. The pure product had the following properties:

Pale yellow crystals, yield: 65%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.43; mp 95–96°C; IR (Nujol), cm^{-1}: 1189 (P=O), 1440, 1461 (Ph), 1612 (C=C), 1944 (C=C=C).

^1H NMR ($CDCl_3$, δ): 1.43 (d, J_{HP} 6.2 Hz, 6H, 2Me), 5.24 (dd, J_{trans} = 15.7 Hz,J_{HP} = 5.7 Hz, 1H, P−CH_a=CH_aH_b), 5.61 (dd, J_{cis} = 10.2 Hz, J_{HP} = 5.9 Hz, 1H, P−CH_a=CH_aH_b), 6.25 (m, 1H, P−CH_a=CH_aH_b), 7.42–7.78 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, δ): 19.0 (J = 5.6 Hz), 97.6 (J = 182.0 Hz), 99.2 (J = 7.8 Hz), 118.8 (J = 7.6 Hz), 129.4 (J = 7.3 Hz), 209.8, 127.2–131.8 (2Ph). ^{31}P NMR ($CDCl_3$, δ): 31.5. $C_{19}H_{19}OP$ (280.32). Calcd.: C 77.52, H 6.51; found: C 77.47, H 6.55.

*General Procedure for the Electrophilic Cyclization Reactions of Diphenyl 3-Methylhexa-1,3,4-trien-3-yl Phosphine Oxide **2***

To a solution of triene **2** (2.80 g, 10 mmol) in dry dichloromethane (20 mL) at −20°C, a solution of electrophilic reagent (sulfuryl chloride, bromine, benzenesulfanyl chloride, or bromide, benzeneselanyl chloride or bromide) (10 mmol) in the same solvent (10 mL) was added dropwise with stirring. The reaction mixture was stirred for 2 h at the same temperature and for 4 h at rt. The solvent was removed using a rotatory evaporator, and the residue was purified by column chromatography on silica gel (Kieselgel Merck 60 F_{254}) with ethyl acetate/hexane.

*4-Chloro-5,5-dimethyl-2,2-diphenyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Chloride (**3a**).* Pale yellow oil, yield: 76%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.83; IR (neat, cm^{-1}): 1445, 1476 (Ph), 1577, 1616 (C=C). ^1H NMR ($CDCl_3$, δ): 1.77 (s, 6H, 2Me), 5.33 (dd, J_{trans} = 14.8 Hz, J_{HP} = 5.8 Hz, 1H, CH_a=CH_aH_b), 6.07 (dd, J_{cis} = 8.9 Hz, J_{HP} = 5.5 Hz, 1H, CH_a=CH_aH_b), 7.32 (m, 1H, CH_a=CH_aH_b), 7.62–8.25 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, δ): 28.9, 97.8 (J = 12.8 Hz), 125.3 (J = 7.0 Hz), 129.4 (J = 7.2 Hz), 140.5 (J = 50.8 Hz), 164.3 (J = 33.2 Hz), 111.9–137.4 (2Ph). ^{31}P NMR ($CDCl_3$, δ): 77.2. $C_{19}H_{19}OPCl_2$ (365.25). Calcd.: C 62.48, H 5.24; found: C 62.40, H 5.27.

*4-Bromo-5,5-dimethyl-2,2-diphenyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Bromide (**3b**).* Pale orange crystals, yield: 78%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.81; mp 133–134°C; IR (Nujol, cm^{-1}): 1440, 1479 (Ph), 1580, 1615 (C=C). ^1H NMR ($CDCl_3$, δ): 1.86 (s, 6H, 2Me), 5.45 (dd, J_{trans} = 15.3 Hz, J_{HP} = 6.0 Hz, 1H, CH_a=CH_aH_b), 5.79 (dd, J_{cis} = 9.4 Hz, J_{HP} = 5.8 Hz, 1H, CH_a=CH_aH_b), 6.76 (m, 1H, CH_a=CH_aH_b), 7.68–8.32 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, δ): 27.9, 100.7 (J = 13.2 Hz), 129.4 (J = 6.7 Hz), 132.0 (J = 7.3 Hz), 135.1 (J = 51.3 Hz), 151.3 (J = 32.0 Hz), 113.4–130.4 (2Ph). ^{31}P NMR ($CDCl_3$, δ): 80.7. $C_{19}H_{19}OPBr_2$ (454.18). Calcd.: C 50.25, H 4.22; found: C 50.32, H 4.17.

*3-(Diphenylphosphinoyl)-2-isopropyl-thiophene (**4**).* Yellow oil: 55% (when PhSCl is the reagent), 52% (when PhSBr is the reagent). Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.60. IR (neat, cm^{-1}): 1160 (P=O), 1439, 1486 (Ph), 1464, 1551 (thiophene). ^1H NMR ($CDCl_3$, δ): 1.38 (d, J_{HP} = 6.4 Hz, 6H, 2Me), 2.82 (m, 1H, $CHMe_2$), 6.85 (dd, J_{HH} = 5.1 Hz, J_{HP} = 4.1 Hz, 1H, SCH=CH), 7.09 (dd, J_{HH} = 5.3 Hz, J_{HP} = 5.3 Hz, 1H, SCH=CH), 7.1–7.73 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, δ): 20.4, 36.2 (J = 7.8 Hz), 130.4 (J = 8.3 Hz), 133.8 (J = 8.0 Hz), 134.9 (J = 122.8 Hz), 161.8 (J = 15.5 Hz), 129.1–136.8 (2Ph). ^{31}P NMR ($CDCl_3$, δ): 29.3. $C_{19}H_{19}OPS$ (326.41). Calcd.: C 69.91, H 5.87; found: C 70.02, H 5.79.

*5,5-Dimethyl-2,2-diphenyl-4-phenylsulfanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Chloride (**5a**).* Pale orange oil, yield: 14%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.79; IR (neat, cm^{-1}): 1436, 1473 (Ph), 1579, 1620 (C=C). ^1H NMR

($CDCl_3$, δ): 1.80 (s, 6H, 2Me), 5.47 (dd, J_{trans} = 15.1 Hz, J_{HP} = 5.4 Hz, 1H, CH_a=CH_aH_b), 6.21 (d, J_{cis} = 9.0 Hz, J_{HP} = 5.7 Hz, 1H, CH_a=CH_aH_b), 7.42 (m, 1H, CH_a=CH_aH_b), 7.04–8.10 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, δ): 31.2 (J = 8.2 Hz), 33.0 (J = 8.2 Hz), 87.1 (J = 13.1 Hz), 118.9 (J = 7.0 Hz), 123.2 (J = 7.7 Hz), 144.7 (J = 50.2 Hz), 166.2 (J = 32.7 Hz), 111.5–138.9 (3Ph). ^{31}P NMR ($CDCl_3$, δ): 79.4. $C_{25}H_{24}OPSCl$ (438.97). Calcd.: C 68.40, H 5.51; found: C 68.33, H 5.59.

*5,5-Dimethyl-2,2-diphenyl-4-phenylsulfanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Bromide (***5b***).* Orange oil, yield: 13%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.66; IR (neat, cm^{-1}): 1441, 1476 (Ph), 1587, 1618 (C=C). ^{1}H NMR ($CDCl_3$, δ): 1.80 (s, 6H, 2Me), 5.44 (dd, J_{trans} = 14.6 Hz, J_{HP} = 5.3 Hz, 1H, CH_a=CH_aH_b), 6.17 (d, J_{cis} = 9.2 Hz, J_{HP} = 5.5 Hz, 1H, CH_a=CH_aH_b), 7.34 (m, 1H, CH_a=CH_aH_b), 7.07–8.07 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, δ): 31.0 (J = 8.0 Hz), 32.9 (J = 8.0 Hz), 89.3 (J = 13.3 Hz), 124.0 (J = 6.8 Hz), 127.4 (J = 7.7 Hz), 149.6 (J = 51.1 Hz), 171.5 (J = 32.4 Hz), 114.4–139.4 (3Ph). ^{31}P NMR ($CDCl_3$, δ): 83.2. $C_{25}H_{24}OPSBr$ (483.38). Calcd.: C 62.11, H 5.00; found: C 62.23, H 5.09.

*3-(Diphenylphosphinoyl)-2-isopropyl-selenophene (***6***).* Pale orange oil, yield: 53% (when PhSeCl is the reagent), 50% (when PhSeBr is the reagent). Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.58; IR (neat, cm^{-1}): 1170 (P=O), 1435, 1485 (Ph). ^{1}H NMR ($CDCl_3$, δ): 1.34 (d, J_{HH} = 6.7 Hz, 6H, 2Me), 2.82 (m, 1H, $CHMe_2$), 7.14 (m, 1H, SeCH=CH), 7.72 (m, 1H, SeCH=CH), 6.81–7.72 (m, 10H, 2Ph). ^{13}C NMR ($CDCl_3$, δ): 19.2 (J = 3.8 Hz), 35.8 (J = 4.1 Hz), 132.7 (J = 8.2 Hz), 135.8 (J = 17.5 Hz), 136.2 (J = 125.8 Hz), 167.7 (J = 14.3 Hz), 127.1–132.8 (2Ph). ^{31}P NMR ($CDCl_3$, δ): 28.8. $C_{19}H_{19}OPSe$ (373.31). Calcd.: C 61.13, H 5.13; found: C 61.19, H 5.09.

*5,5-Dimethyl-2,2-diphenyl-4-phenylselanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Chloride (***7a***).* Pale orange oil: 14%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.76; IR (neat, cm^{-1}): 1449, 1477 (Ph), 1581, 1622 (C=C). ^{1}H NMR ($CDCl_3$, δ): 1.61 (s, 6H, 2Me), 5.18 (dd, J_{trans} = 14.8 Hz, J_{HP} = 4.8 Hz, 1H, CH_a=CH_aH_b), 5.91 (dd, J_{cis} = 8.8 Hz, J_{HP} = 5.6 Hz, 1H, CH_a=CH_aH_b), 7.18 (m, 1H, CH_a=CH_aH_b), 6.97–8.61 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, δ): 27.3 (J = 7.8 Hz), 29.1 (J = 7.8), 93.8 (J = 15.7 Hz), 118.3 (J = 6.9 Hz), 126.6 (J = 7.3 Hz), 148.6 (J = 51.0 Hz), 169.4 (J = 16.3 Hz), 111.5–138.9 (3Ph). ^{31}P NMR ($CDCl_3$, δ): 82.4. $C_{25}H_{24}OPSeCl$ (485.86). Calcd.: C 61.80, H 4.98; found: C 61.93, H 5.09.

*5,5-Dimethyl-2,2-diphenyl-4-phenylselanyl-3-vinyl-2,5-dihydro-1,2-oxaphosphol-2-ium Bromide (***7b***).* Orange oil: 13%. Eluent for TLC: ethyl acetate : hexane = 4:1, R_f 0.69; IR (neat, cm^{-1}): 1452, 1479 (Ph), 1584, 1620 (C=C). ^{1}H NMR ($CDCl_3$, δ): 1.65 (s, 6H, 2Me), 5.14 (dd, J_{trans} = 14.5 Hz, J_{HP} = 4.7 Hz, 1H, CH_a=CH_aH_b), 5.86 (dd, J_{cis} = 8.9 Hz, J_{HP} = 5.7 Hz, 1H, CH_a=C H_aH_b), 7.09 (m, 1H, CH_a=CH_aH_b), 7.02–8.72 (m, 15H, 3Ph). ^{13}C NMR ($CDCl_3$, δ): 27.0 (J = 7.6 Hz), 28.8 (J = 7.6 Hz), 95.6 (J = 15.9 Hz), 126.6 (J = 6.9 Hz), 136.7 (J = 7.5 Hz), 152.1 (J = 50.1 Hz), 171.2 (J = 16.6 Hz), 109.7–137.5 (3Ph). ^{31}P NMR ($CDCl_3$, δ): 87.0. $C_{25}H_{24}OPSeBr$ (530.27). Calcd.: C 56.62, H 4.56; found: C 56.56, H 4.57.

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